

LA-UR-20-21659

Approved for public release; distribution is unlimited.

Title: Selective hydrothermal extraction of lanthanides: mimicking natural ore-forming processes

Author(s): Migdisov, Artaches
Strzelecki, Andrew Charles
Boukhalfa, Hakim
Sauer, Kirsten Benedict
Nisbet, Haylea Dawn
Velizhanin, Kirill A.
Currier, Robert Patrick

Intended for: Report

Issued: 2020-02-20

Disclaimer:

Los Alamos National Laboratory, an affirmative action/equal opportunity employer, is operated by Triad National Security, LLC for the National Nuclear Security Administration of U.S. Department of Energy under contract 89233218CNA000001. By approving this article, the publisher recognizes that the U.S. Government retains nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or to allow others to do so, for U.S. Government purposes. Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy. Los Alamos National Laboratory strongly supports academic freedom and a researcher's right to publish; as an institution, however, the Laboratory does not endorse the viewpoint of a publication or guarantee its technical correctness.

Selective hydrothermal extraction of lanthanides: mimicking natural ore-forming processes

A. Migdisov; A.C. Strzelecki; H. Boukhalfa; K. Sauer; H. Nisbet; K. Velizhanin; R. P. Currier



20190057DR Progress Appraisal

February 24, 2020



Managed by Triad National Security, LLC for the U.S. Department of Energy's NNSA

Why Lanthanides? – Rare Earth Crisis

Periodic Table of the Elements



hybrid vehicles, rechargeable batteries, wind turbines, cell phones, flat screen display panels, compact fluorescent light bulbs, laptop computers, disk drives, catalytic converters

China: controls 97% of the global REE market

REE consumption in US: 20,000 metric ton in 2018

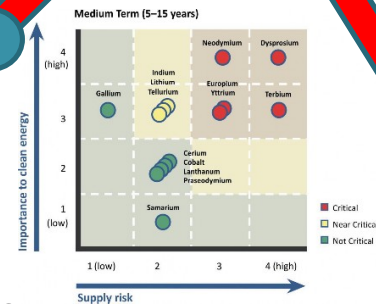
2014: USGS Mineral Resources report “The Rare-Earth Elements - Vital to Modern Technologies and Lifestyles”

2013: DOE “Critical materials institute” hub was created based on the Ames Lab (EERE, AM)

2011: DOE “Critical materials strategy” report released

2006: China enforced quotas for the export of REE; 2,000-5,000% increase of prices for REE

2015: China lost its case at WTO; Quotas are removed; Prices returned back to pre-2006 level; US companies are broke; production of REE stopped



Sources of the current crisis (second wave)

1. Low labor and production cost in China:

Time	LIGHT RARE EARTH METALS	Last Price	Units
09 May 2018	Lanthanum metal $\geq 99\%$	6.00	US\$/kg
09 May 2018	Cerium metal $\geq 99\%$	6.10	US\$/kg
09 May 2018	Praseodymium metal $\geq 99\%$	128.00	US\$/kg
09 May 2018	Neodymium metal $\geq 99.5\%$	70.00	US\$/kg
09 May 2018	Samarium metal $\geq 99.9\%$	15.50	US\$/kg
Time	HEAVY RARE EARTH METALS	Last Price	Units
09 May 2018	Gadolinium metal 99.9%	46.00	US\$/kg
09 May 2018	Terbium metal $\geq 99.9\%$	665.00	US\$/kg
09 May 2018	Dysprosium metal $\geq 99\%$	278.00	US\$/kg
09 May 2018	Erbium metal $\geq 99.9\%$	111.85	US\$/kg
09 May 2018	Yttrium metal $\geq 99.9\%$	37.50	US\$/kg
09 May 2018	Scandium metal 99.9%	3,617.00	US\$/kg
09 May 2018	Mischmetal $\geq 99\%$	6.00	US\$/kg

REE concentrate value
(after primary extraction from feed stock):

Hydrochloric Acid, Technical:

Sulfuric Acid, Technical:

5 to 15 \$/kg

\$77.00 / 2.5 l

\$92.04 / 2.5 l

REE oxide	Bastnaesite (wt.%)	Xenotime (wt%)	Monazite (wt%)
La ₂ O ₃	33.8	-	15.29
Ce ₂ O ₃	49.6	-	31.21
Pr ₂ O ₃	4.1	-	3.57
Nd ₂ O ₃	11.2	0.17	8.84
Sm ₂ O ₃	0.9	0.49	2.02
Eu ₂ O ₃	0.1	0.04	0.01
Gd ₂ O ₃	0.2	1.89	0.05
Tb ₂ O ₃	trace	0.6	-
Dy ₂ O ₃	trace	5.15	-
Ho ₂ O ₃	trace	1.06	-
Er ₂ O ₃	trace	3.86	-
Tm ₂ O ₃	trace	0.7	-
Yb ₂ O ₃	trace	4.1	0.35
Lu ₂ O ₃	trace	0.52	-
Y ₂ O ₃	trace	46.49	-
ThO ₂	trace	0.38	1.65
UO ₂	trace	0.96	0.36

2. Environmental regulations in US:

Conventional extraction and purification of REE:

Extensive use of
**organic solvents,
strong acids and
bases**



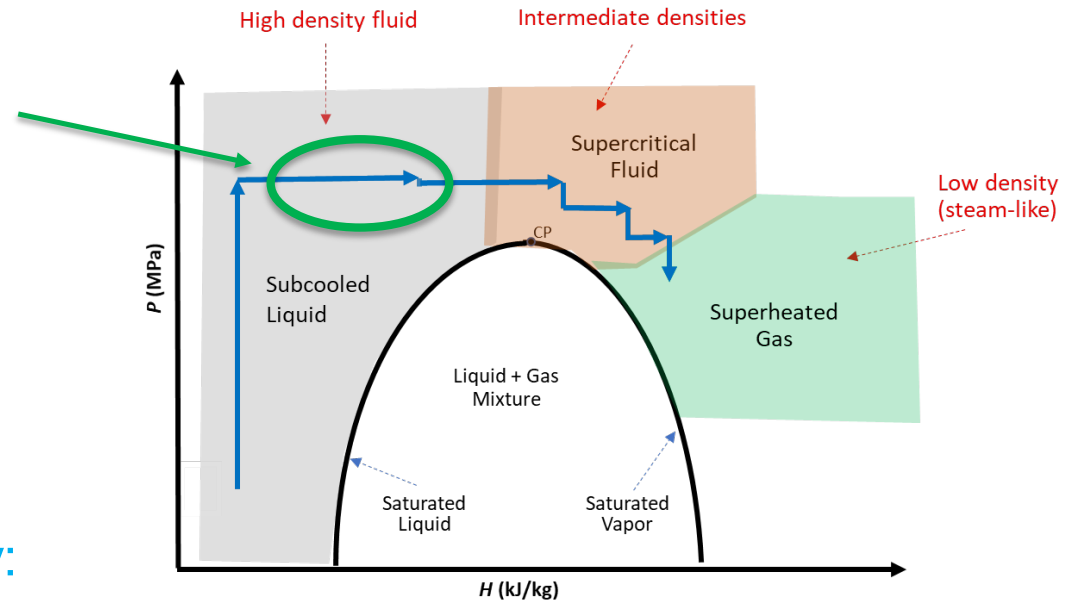
U and Th closely accompany Ln in nature, are co-extracted and concentrated by conventional technologies: **need to invest in remediation of rad waste**



Technical Goals

Focus: co-production of REE
(Lanthanides + Y + Sc)
combined with desalinization

Aim for new technology:



1. Avoid investing in extraction of cheap **LREE**, extract **M/HREE** only → **increase the value of the intermediate/final product**
2. Exclude extraction and concentration of **U** and **Th** → **avoid investment in rad remediation**
3. Maximize **environmental friendliness** of the technology

Hints from the nature

Nature does not use expensive reagents or strong acids to extract and concentrate REE to ore bodies– not much more than **hot water** and abundant ligands!

Known natural depositional (concentration) mechanisms:

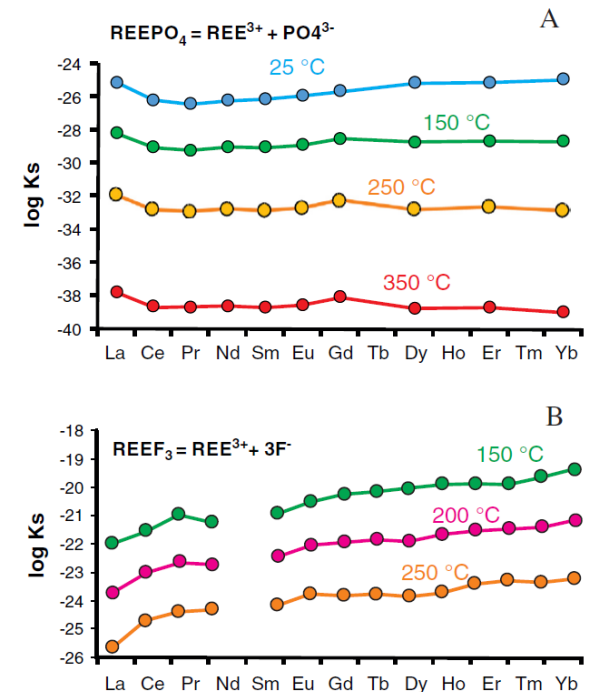
Extremely low solubility of REE phosphates and fluorides. Just traces of F or PO_4 lead to REE precipitation



Solubilities are so low that REE precipitation is preferential against other elements (selective)



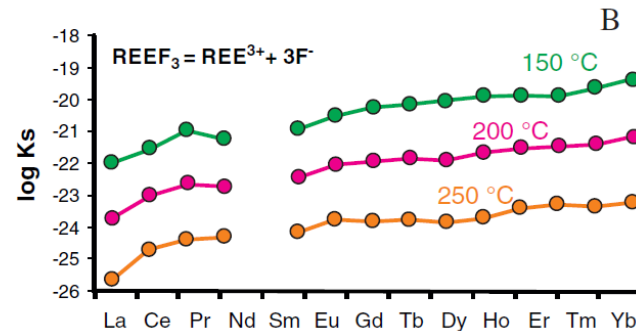
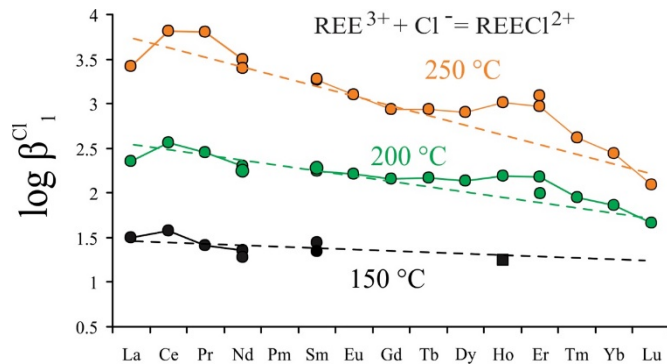
Solubilities are retrograde (decrease with increasing temperature): most efficient at higher T



Migdisov et al. *Chem. Geol.* **439**, 13–42 (2016).

Hints from the nature

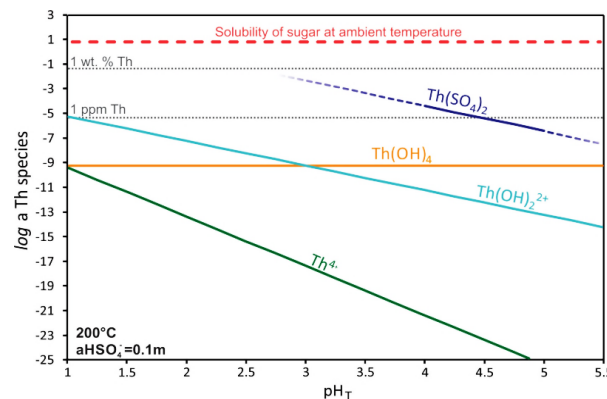
LREE, M/HREE, U, and Th are known to fractionate in ore forming systems:



Due to different solubility of solid end members

Due to different stability of aqueous species (at high T)

Extremely rare, but documented case -
deposits highly enriched with M/HREE: Lodfal, Namibia; Brown Range, Australia

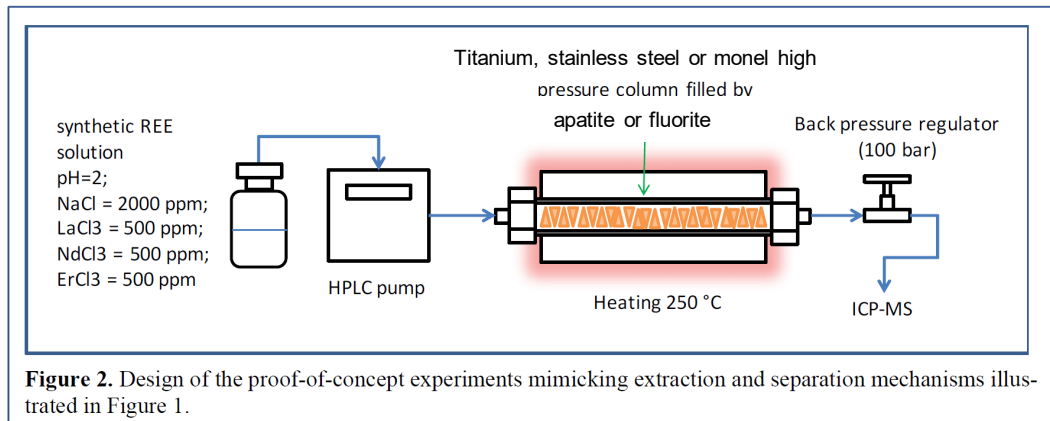


Migdisov et al., Hydrothermal transport, deposition, and fractionation of the REE: Experimental data and thermodynamic calculations. *Chem. Geol.* **439**, 13–42 (2016).

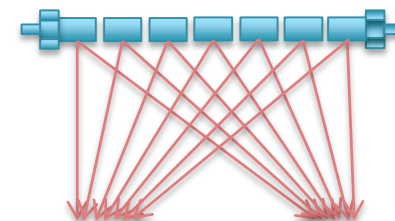
Migdisov et al., Fractionation of REE, U, and Th in natural ore-forming hydrothermal systems: Thermodynamic modeling. *The Journal of Chemical Thermodynamics* **128**, 305–319 (2019)

Nisbet, H. et al. Challenging the Th immobility paradigm—Scientific reports **9** (1), 1–6 (2019)

Method



Post-experiment treatment



XRD; SEM
(mineral
composition)

XRF
(chemical
composition)



High Pressure Pumps



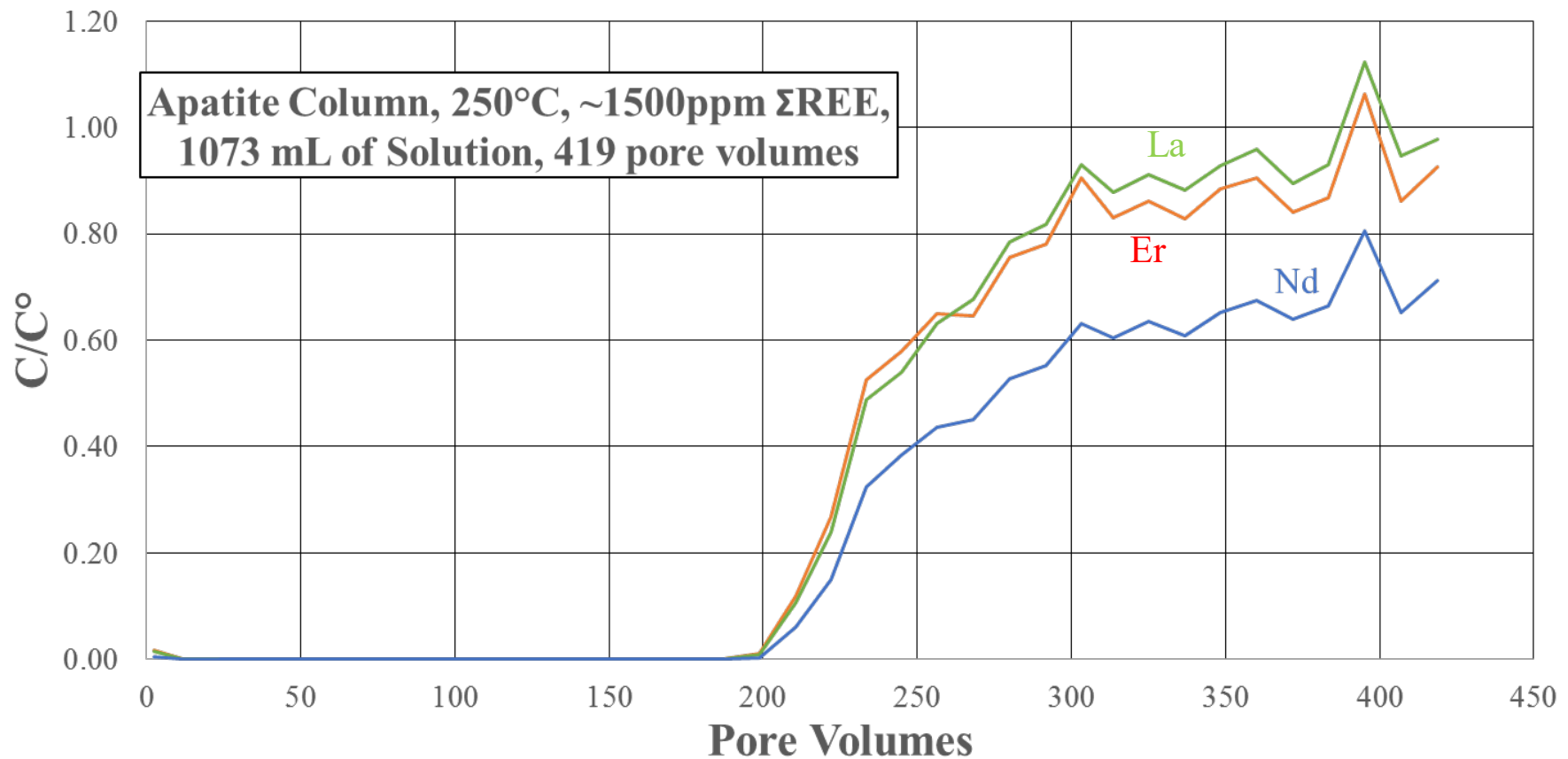
Oven



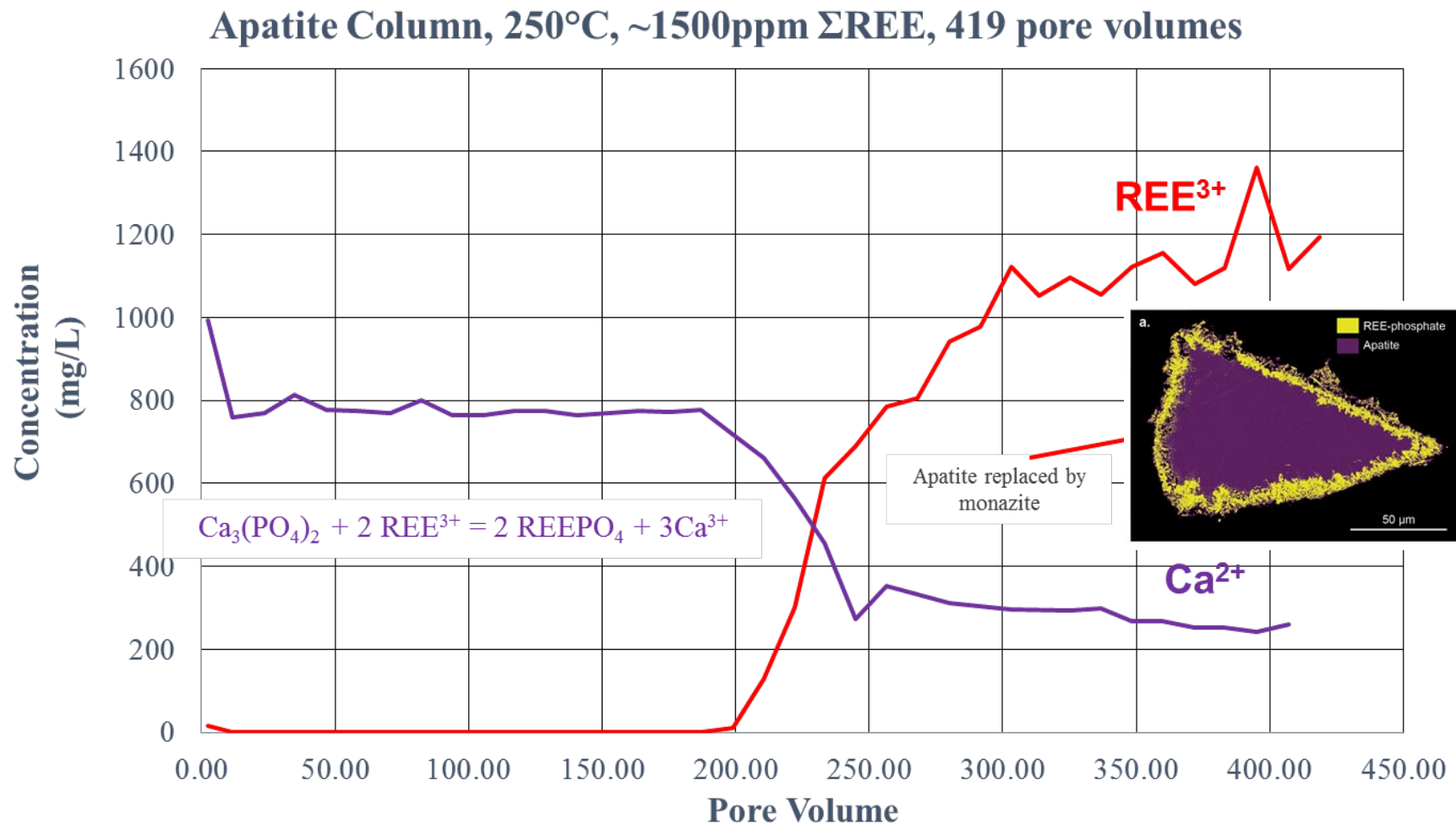
Fraction collector

Apatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$) – filled columns

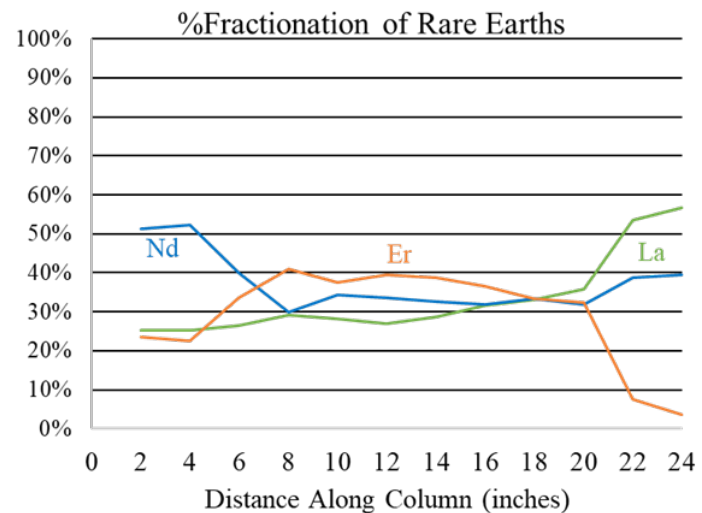
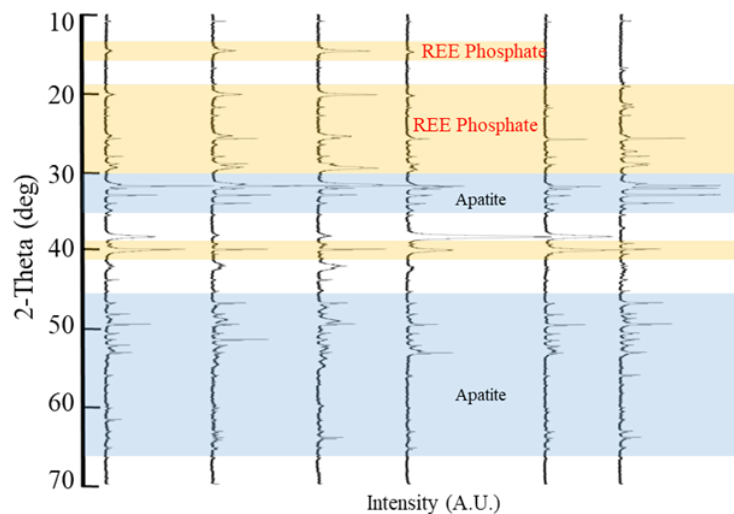
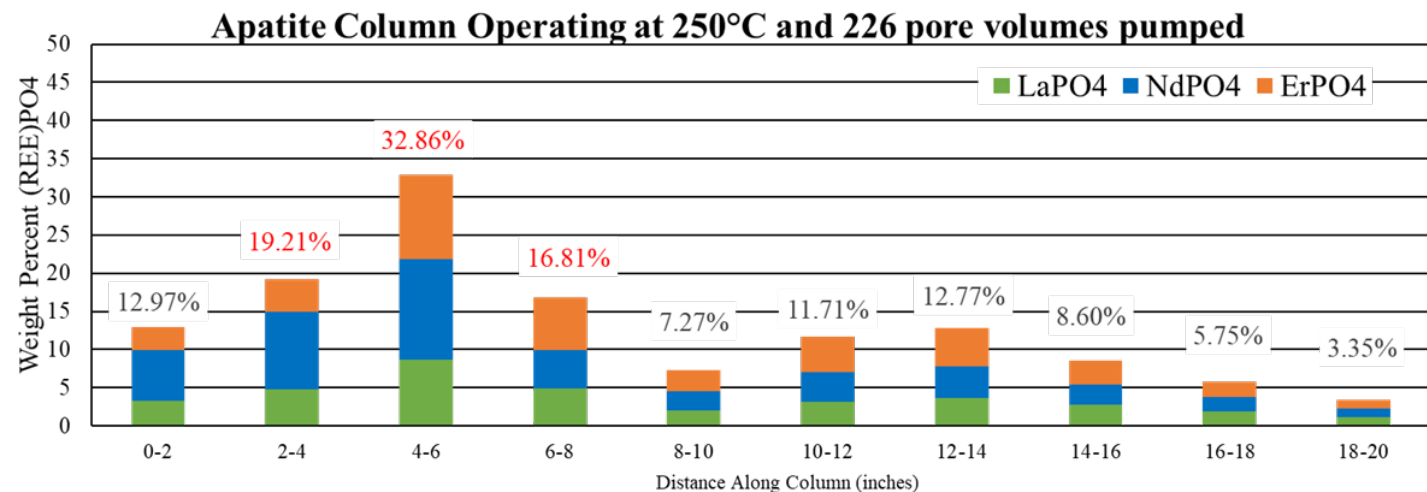
Apatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$) – filled columns



Apatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$) – filled columns

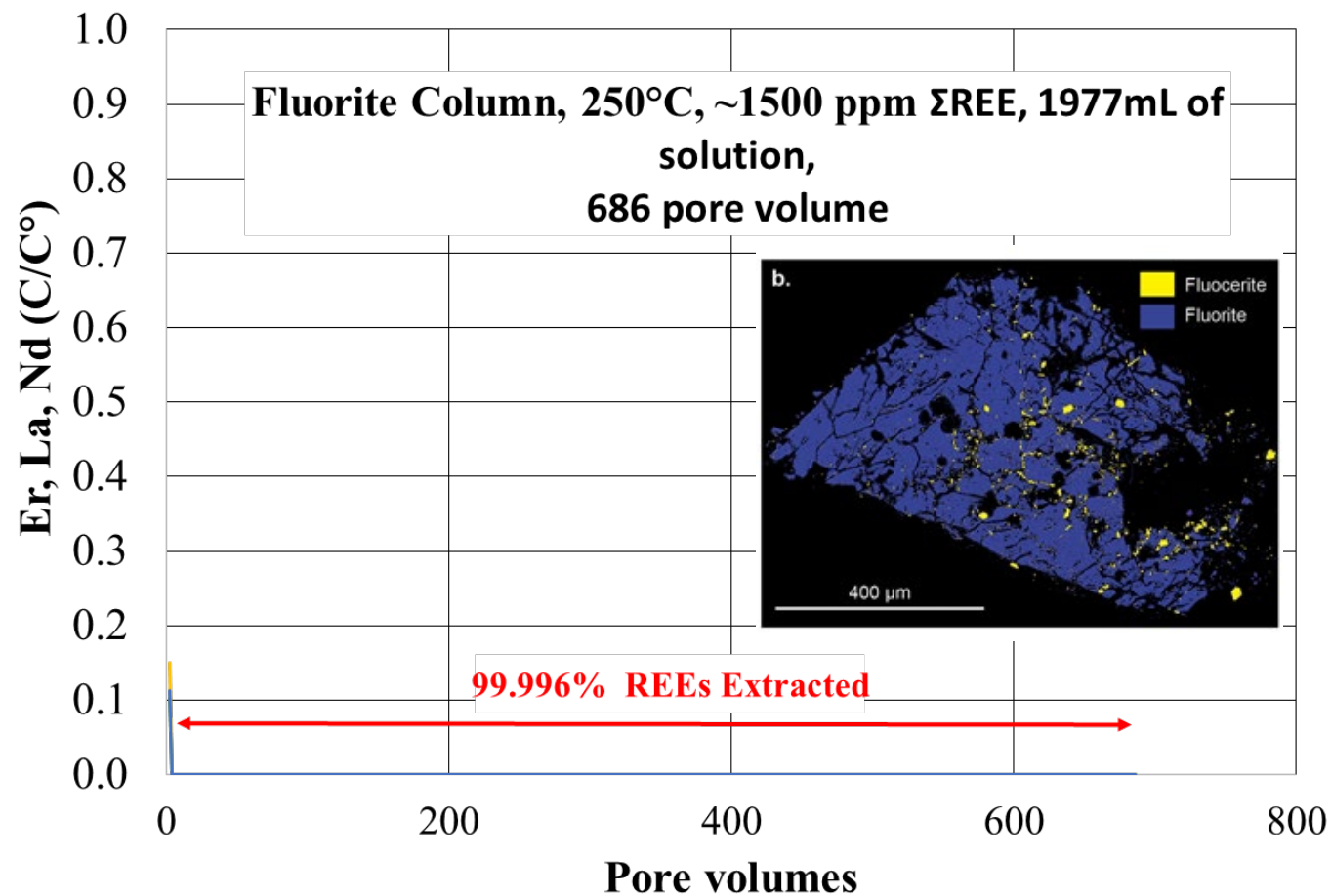


Apatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$) – filled columns

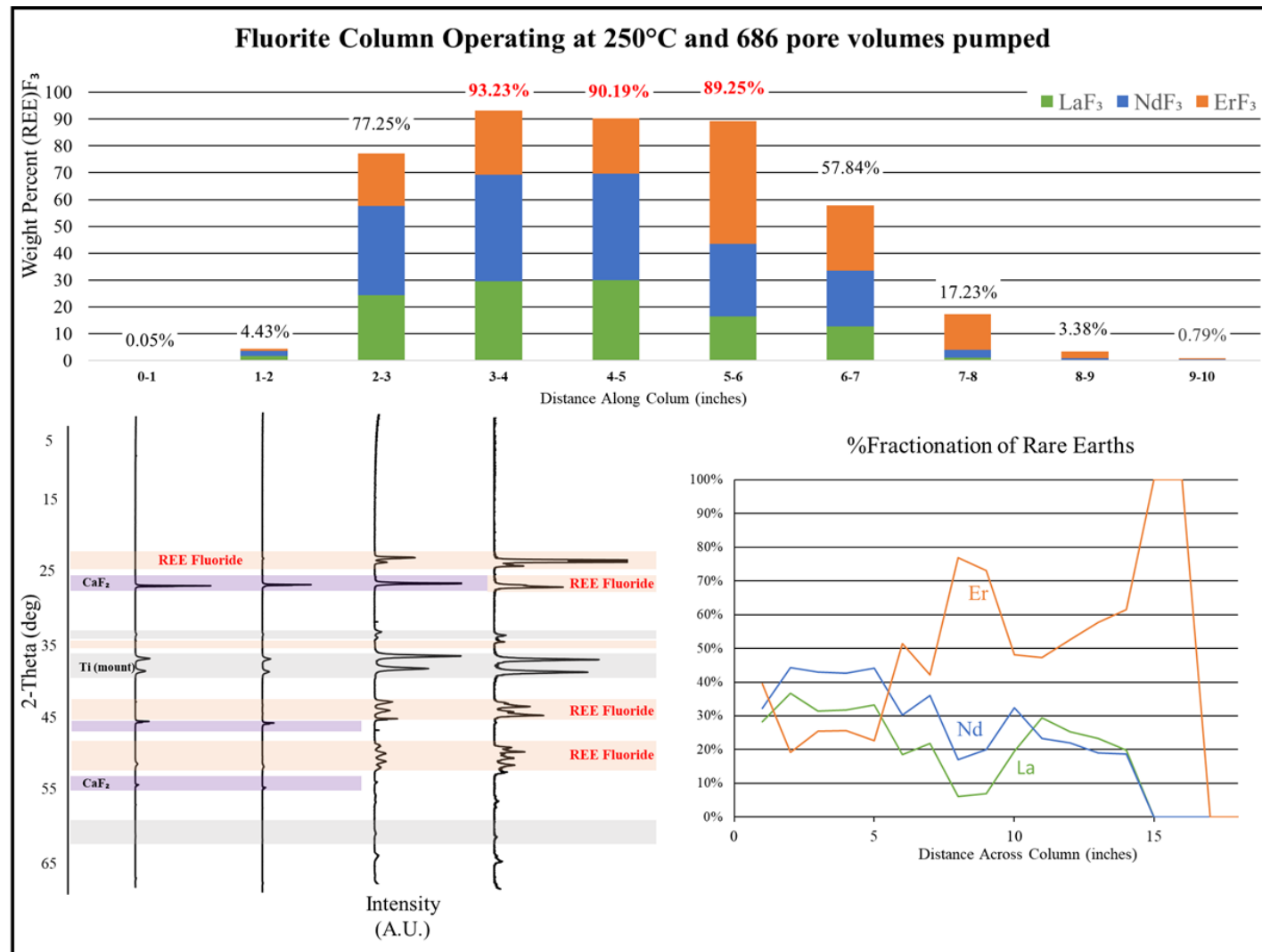


Fluorite (CaF_2) - filled columns

Fluorite (CaF_2) - filled columns



Fluorite (CaF_2) - filled columns

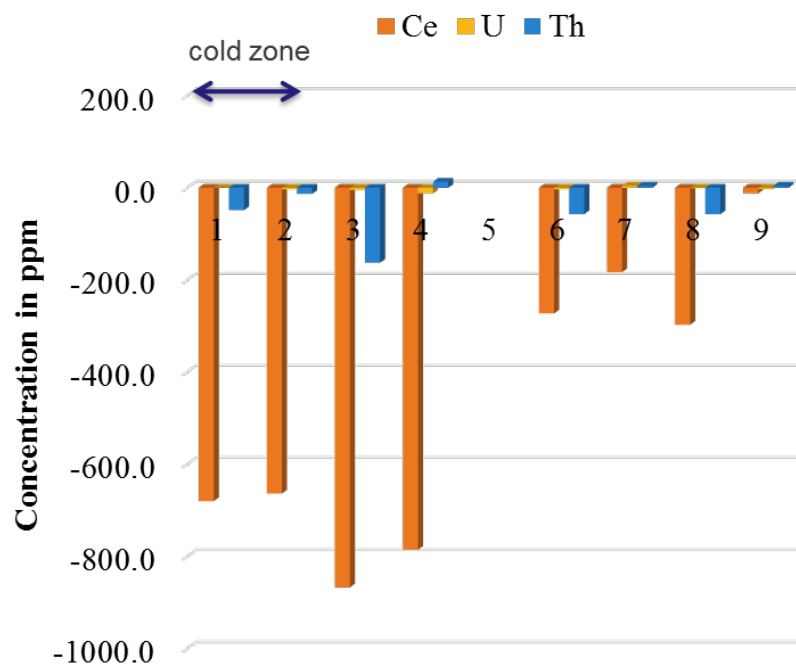


Other elements beside La, Nd, and Er

Other elements (U,Th)

Table 2. Detailed elemental composition of apatite used as column fill material.

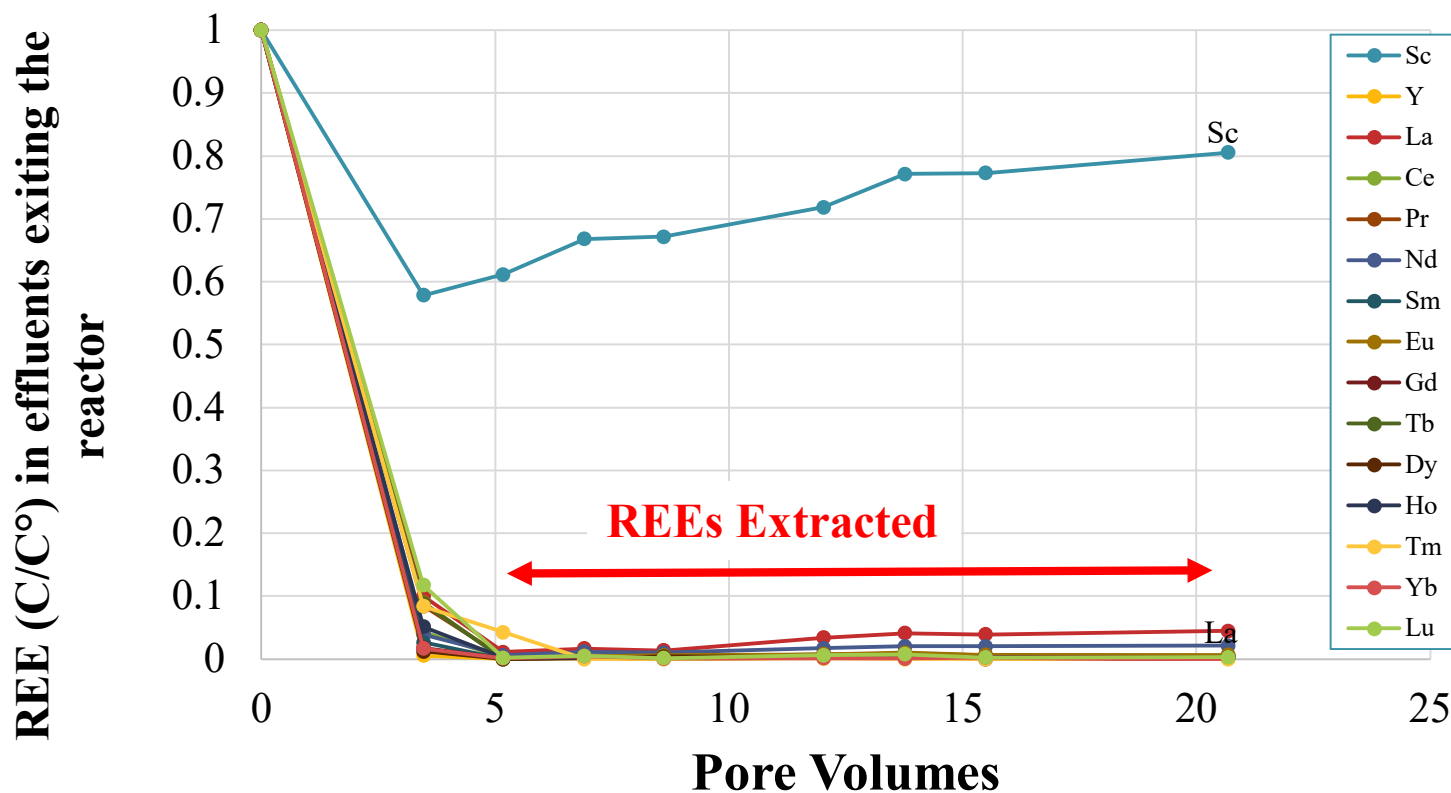
Element I.D.	% or PPM
Na ₂ O %	0.222
MgO %	0.07
Al ₂ O ₃ %	0.196
SiO ₂ %	9.1
P ₂ O ₅ %	33.8
CaO %	54.7
V ppm	20
Cr ppm	179
NiO	0.004
Ni ppm	30
Cu ppm	15
Sr ppm	631
Y ppm	449
Zr ppm	150
Pb ppm	53
La ppm	2404.5
Ce ppm	5120.6
Pr ppm	452.0
Sm ppm	119.0
Gd ppm	138.7
Nd ppm	1594.7
Er ppm	82.201
Th ppm	2144.3
U ppm	71.2
LOI %	0.18
Total %	100.2



Other elements (Sc)

- » Extraction of REE elements from an acid mine drainage sample from a coal mining plant

Bethel AMD Pump Solution, pH 2, 250°C



Conclusion

1. Hydrothermal-based technology (with fluorite) extracts from aqueous feedstock M/HREE selectively
2. Hydrothermal approach permits to avoid extracting and concentrating U and Th
3. The technology is patented (U.S. provisional patent application No. 62/859,428)
4. Manuscript: *Nature Geoscience*, under review

Path forward

1. REE **always** occur as a group of elements – not as a single representative of the Ln group → they **never** form **pure solid end members**, but always **solid solutions**
 - ✓ Properties of REE solid solutions are extremely poorly known
 - ✓ This knowledge is required to tune up the extraction technology based on precipitation of solids or solid/solutions
 - ✓ Re: See the **poster of Nisbet**

Path forward

2. Sc – an outlaw
in the REE group,... though a
very attractive outlaw

- ✓ Properties of Sc are
effectively unmapped
in aqueous, gas, and
solid phases

Time	LIGHT RARE EARTH METALS	Last Price	Units
09 May 2018	Lanthanum metal $\geq 99\%$	6.00	US\$/kg
09 May 2018	Cerium metal $\geq 99\%$	6.10	US\$/kg
09 May 2018	Praseodymium metal $\geq 99\%$	128.00	US\$/kg
09 May 2018	Neodymium metal $\geq 99.5\%$	70.00	US\$/kg
09 May 2018	Samarium metal $\geq 99.9\%$	15.50	US\$/kg
Time	HEAVY RARE EARTH METALS	Last Price	Units
09 May 2018	Gadolinium metal 99.9%	46.00	US\$/kg
09 May 2018	Terbium metal $\geq 99.9\%$	665.00	US\$/kg
09 May 2018	Dysprosium metal $\geq 99\%$	278.00	US\$/kg
09 May 2018	Erbium metal $\geq 99.9\%$	111.85	US\$/kg
09 May 2018	Yttrium metal $\geq 99.9\%$	37.50	US\$/kg
09 May 2018	Scandium metal 99.9%	3,617.00	US\$/kg
09 May 2018	Mischmetal $\geq 99\%$	6.00	US\$/kg

- ✓ Understanding of the behavior of this element is required for its
efficient extraction
- ✓ Re: See the **poster of Alcorn**